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Nickel-catalyzed dynamic kinetic cross-electrophile coupling of benzylic alcohols and alkenyl triflates†

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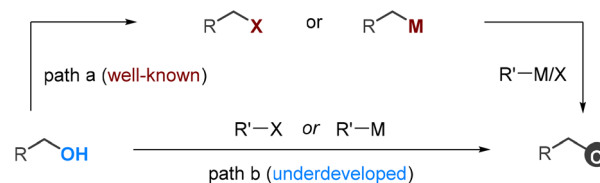
The direct deoxy-functionalization of alcohols through cross-coupling is synthetically appealing but remains a challenging task. In this manuscript, we report a dynamic kinetic cross-electrophile coupling reaction between benzylic alcohols and alkenyl triflates. This mild reaction enables the replacement of the alcohol group with an alkenyl functionality, yielding versatile benzyl-substituted cyclic alkenes. The production of cyclic alkenes makes the method orthogonal to the existing reductive coupling methodologies, which are mainly effective in producing acyclic derivatives. Functional groups such as ester, phenol, indole, heterocycle, and boronic ester are tolerated.

Introduction

Alcohols are readily available functional groups, making them highly desirable for transition-metal-catalyzed C–C coupling reactions. However, due to the high bond dissociation energy of the C–OH bond, these processes usually involve multistep operations, requiring their pre-functionalization to activated electrophilic or organometallic species (Scheme 1, path a).¹ These multistep sequences are costly and time-consuming, and they always restrict the tolerance of functional groups. Consequently, new methods that allow for the direct functionalization of alcohols are in high demand, yet they are currently underdeveloped (Scheme 1, path b).^{2,3}

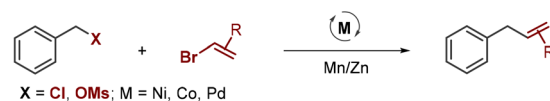
There are only a limited number of studies that demonstrate the deoxygenative C–C coupling of benzylic alcohols. For instance, the Shi group reported transition-metal-catalyzed arylation reactions using Grignard reagents and aryl boroxines as coupling partners.⁴ Ukaji *et al.* reported titanium-assisted and nickel-catalyzed cross-electrophile coupling of benzyl alcohols with aryl and alkenyl halides.⁵ Very recently, our group reported a dynamic kinetic cross-coupling strategy for direct functionalization of alcohols.⁶ This protocol utilizes the slow equilibrium reaction between alcohols and dimethyl oxalate (DMO); the *in situ*-formed oxalates are available for the coupling reactions. While the feasibility of this strategy was demonstrated through a deoxyarylation reaction, its potential in organic synthesis remains largely unexplored.

Allylbenzenes are important structural motifs widely found in naturally-occurring molecules. Catalytic cross-electrophile coupling between benzyl and alkenyl electrophiles offers a convenient access to these compounds.^{7–9} Initially, these studies focus mainly on the reactions involving benzyl halides (Scheme 2a).⁹ Very recently, the scope of this chemistry has

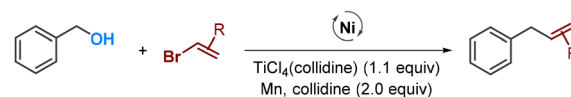


Scheme 1 General approaches for deoxygenative C–C coupling of alcohols by transition metal catalysis.

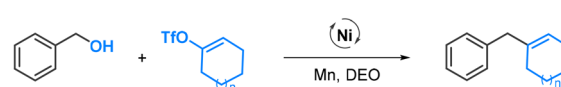
2a TM-catalyzed reductive coupling between benzyl and alkenyl halides (ref. 9)



2b Ti-assisted Ni-catalyzed reductive alkenylation of benzy alcohols (ref. 5b)



2c Dynamic kinetic cross-electrophile alkenylation of benzyl alcohols (this work)



Scheme 2 Cross-electrophile coupling between benzyl and alkenyl electrophiles.

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been extended to benzyl alcohols (Scheme 2b).^{5b} Despite formidable advances, these processes are effective mainly in producing acyclic alkenes using alkenyl bromides as coupling partners. In this manuscript, we report a nickel-catalyzed dynamic kinetic cross-electrophile coupling between benzyl alcohols and alkenyl triflates (Scheme 2c). This method demonstrates the direct conversion of alcohols and easily accessible alkenyl triflates, derived from ketones, into alkenes.⁸ This protocol enables the production of cyclic alkenes, offering an orthogonal approach to existing methodologies.^{5b,9}

Results and discussion

We started our investigations by examining the reaction between alcohol **1a** and alkenyl triflate **2a** (Table 1). Under the conditions of Ni(dppf)Cl₂ (10 mol%), dppf (10 mol%), and phen (2 mol%) in DMF that we had previously established for reductive arylation reactions,⁶ the reaction yielded compound **3a** in a modest 44% yield (Scheme S1 in the ESI†). Our extensive studies revealed that the best result was achieved by using a combination of Ni(dppf)Cl₂ (10 mol%), dtbpy (20 mol%), diethyl oxalate (DEO, 1.5 equiv.), Mn (3.0 equiv.), and DMSO/MeCN (1 : 1). These alternative conditions afforded compound **3a** in an impressive 94% isolated yield (entry 1). The combination of phosphine and nitrogen ligands was found to be crucial for the activation of both alcohols and alkenyl triflates. The use of a single nitrogen (entries 2 and 3) or a phosphine (entry 4) ligand resulted in the recovery of most of these two

substrates. The use of Ni(dppp)Cl₂ provided **3a** in 68% yield (entry 5). The alkenylation reaction in DMF afforded **3a** in 79% yield (entry 6). While performing the reaction in either DMSO or MeCN led to a low yield of **3a**, utilizing DMSO/MeCN (1 : 1) significantly enhanced the reaction efficiency (entries 7 and 8). The reaction with Zn instead of Mn delivered **3a** in 65% yield (entry 9). The use of DMO (dimethyl oxalate) instead of DEO provided **3a** in 82% yield (entry 10). This reagent may affect the efficiency of transesterification of alcohols to oxalates, as well as the activation of oxalates, leading to a slight decrease in the yield. No reaction was observed in the absence of DEO, a nickel catalyst, or a reducing agent (entry 11). While the phen ligand **L1** was found to be essential in our prior arylation reaction, it led to the target product in 52% yield. Reactions using bipyridine ligands (**L2–3**) exhibited greater effectiveness, with the best outcome achieved using dtbpy (**L3**). Pybox ligand **L4** and tridentate nitrogen ligands **L5** displayed lower efficacy.

The substrate scope of alcohol was investigated using alkenyl triflate **2a** as a coupling partner (Table 2). Electron-neutral (**1b**), -rich (**1c–j**), and -poor (**1k–n**) benzyl alcohols all coupled well with triflate **2a**. The methoxy groups placed at *para*- (**1c**), *meta*- (**1d**), and *ortho*-positions (**1e**) are tolerated, yielding the desired products in 78–85% yields. The reactions involving electron-poor benzyl alcohols showed moderate yields (**1k–n**). Organosilanes and boronic esters, widely utilized in cross-coupling reactions, were compatible with our conditions and could be incorporated into the coupling products (**1p–s**). The reactions involving heterobenzylic alcohols, including furan (**1t**), thiophene (**1u** and **1v**), pyridine (**1w**), benzothiophene (**1x**), and indole (**1y**), generally afforded the target products in good yields. Additional functionalities such as phenol (**1z**), alkene (**1aa** and **1ab**), amide (**1ac**), and ester (**1ad**) were tolerated.

We then examined the scope of this reaction with respect to alkenyl triflates (Table 3). In addition to six-membered cyclic alkenyl triflates, five- and eight-membered ring derivatives gave the coupling products in 60% and 43% yields, respectively (**2b** and **2c**). The 4- and 5-substituted alkenyl triflates exhibited good coupling efficiency, affording the alkenylation products in yields up to 93% (**2d–j**). A bridged cyclic alkenyl triflate **2k** resulted in a moderate yield. Heterocyclic alkenyl triflates, such as 3,6-dihydro-2H-pyran (**2l**) and 3-piperidine (**2m–o**), were coupled efficiently, delivering the coupling products in 80–95% yields. The reaction could be scaled up to the gram scale without significant loss in efficiency (**2n**). Acyclic alkenyl triflates are presently less effective; the reactions of **2p** and **2q** gave moderate yields of the desired products.

Standard conditions failed to yield the desired products from secondary alcohols. Reducing dtbpy (10 mol%) and adding MgCl₂ (1.2 equiv.) resulted in the formation of coupling products **1ae–ah**, albeit with relatively low yields (Table 4). Tertiary alcohols remain unreactive, likely due to their low efficiency in transesterification.

Late-stage modification of biologically active molecules presents a promising approach for obtaining compounds with modified pharmacological profiles. In this context, benzyl alcohols derived from flufenamic acid and adapalene were suc-

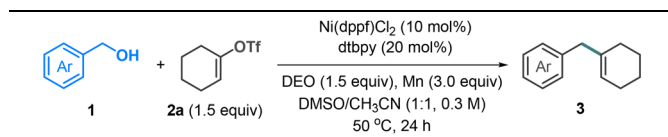
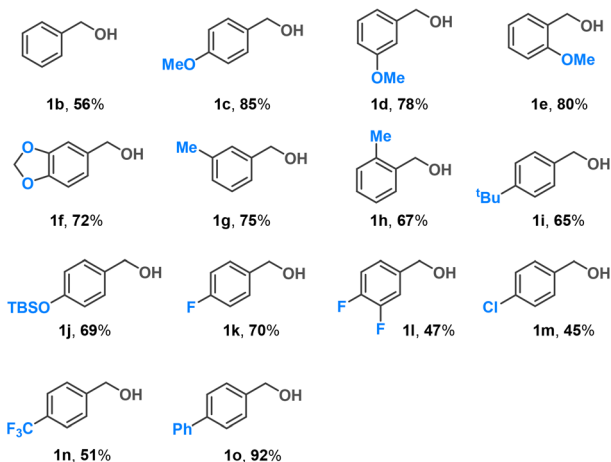
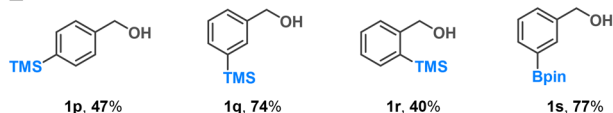
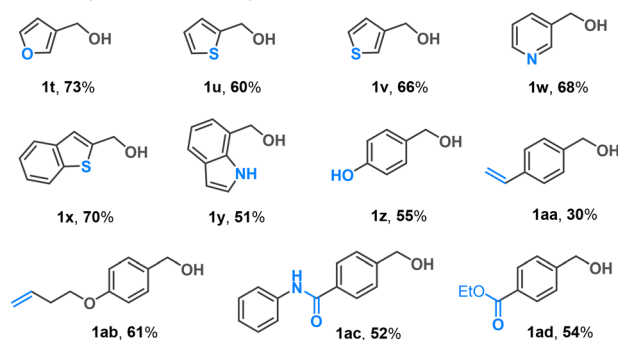
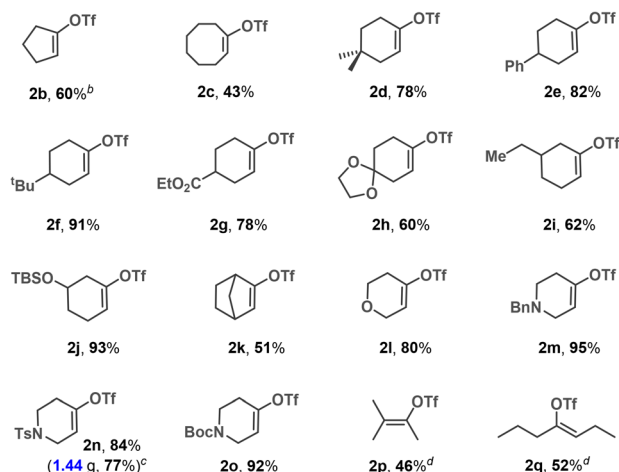
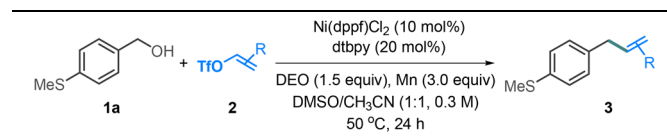
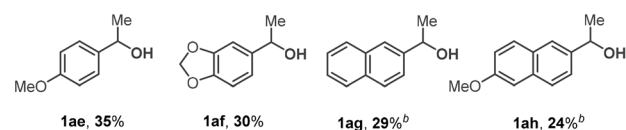
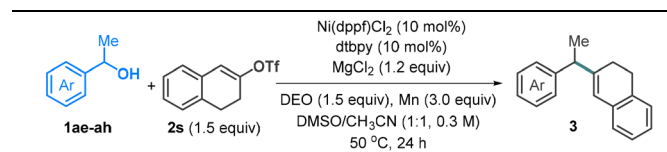
Table 1 Optimization of reaction conditions^a

Entry	Change from standard conditions	3a (%)
1	None	98 (94) ^b
2	NiCl ₂ instead of Ni(dppf)Cl ₂	Trace
3	Ni(COD) ₂ instead of Ni(dppf)Cl ₂	Trace
4	No dtbpy	Trace
5	Ni(dppp)Cl ₂ instead of Ni(dppf)Cl ₂	68
6	DMF	79
7	DMSO	43
8	CH ₃ CN	7
9	Zn instead of Mn	65
10	DMO instead of DEO	82
11	No DEO, Ni or Mn	0

Effect of Ligands:

L1, 52%	L2, 78%	L3, 94%	L4, 24%	L5, 8%

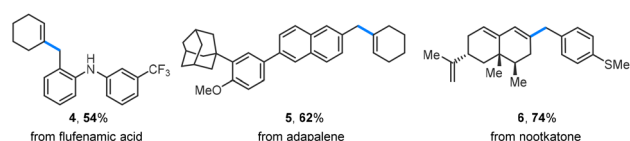
^a Reaction conditions: **1a** (0.1 mmol) and **2a** (0.15 mmol) were used; the yields were determined by NMR analysis using CH₂Br₂ as an internal standard; DEO: diethyl oxalate. ^b Isolated yield in parentheses is obtained from **1a** (0.2 mmol) and **2a** (0.3 mmol).

Table 2 The substrate scope of primary benzyl alcohols^a**Electronic and steric effects****Metalloid substrates****Heterocycles and functionality tolerance**^a **1a** (0.2 mmol) and **2a** (0.3 mmol) were used; isolated yields are given.**Table 3** The substrate scope of alkenyl triflates^a^a **1a** (0.2 mmol) and **2a** (0.3 mmol) were used; isolated yields are given. ^b Reaction at 80 °C. ^c **1a** (5.0 mmol) and **2n** (7.5 mmol) were used. ^d Ni(PCy₃)₂Cl₂ (0.02 mmol), 4,4'-dimethyl-2,2'-bipyridyl (0.04 mmol), dppf (0.02 mmol), and ZrCl₄ (0.04 mmol) were used, and reaction at 30 °C.**Table 4** The substrate scope of secondary benzyl alcohols^a^a **1** (0.2 mmol) and **2s** (0.3 mmol) were used; isolated yields are given. ^b Alkenyl triflate **2a** was used.

cessfully coupled with alkenyl triflates, leading to the formation of alkenes **4** and **5** (Scheme 3). Additionally, a nootkatone-derived triflate underwent a benzylation reaction with a yield of 74% (**6**).

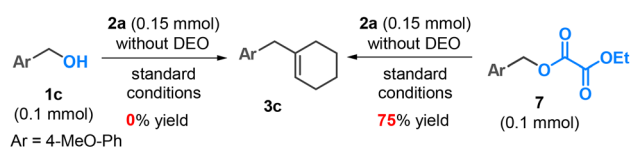
In the absence of DEO, the reaction of **1c** and **2a** under the standard conditions did not give any desired product, indicating the crucial role of DEO in the success of this process (Scheme 4a, left). However, when oxalate **7** was employed, the reaction proceeded efficiently, leading to the formation of **3c** in 75% yield (Scheme 4a, right). These results suggest that an *in situ*-generated oxalate might serve as a key intermediate in this reaction.

Our previous studies revealed that nickel activates the oxalate through a single-electron process,^{6a} while cobalt under-

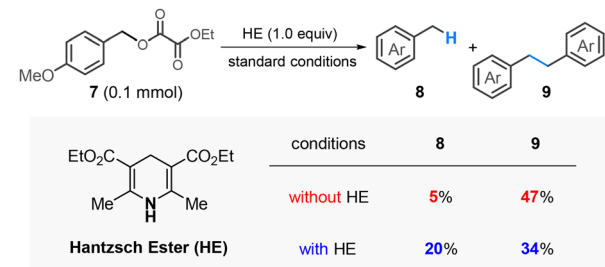
**Scheme 3** Late-stage modification of biologically active molecules. Benzyl alcohols (0.2 mmol) were used, and isolated yields are given.

goes a two-electron oxidative addition.^{6b} To determine the process involved under the current conditions, several control experiments were conducted. (1) Hantzsch ester (HE) has been established as a good hydrogen atom donor capable of trapping carbon radicals.¹⁰ In the presence of HE (1.0 equiv.), the

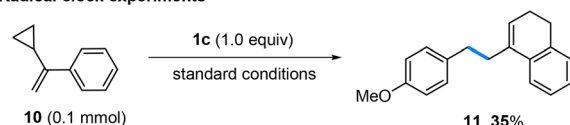
(a) Effect of the oxalate group



(b) Radical trapping experiments



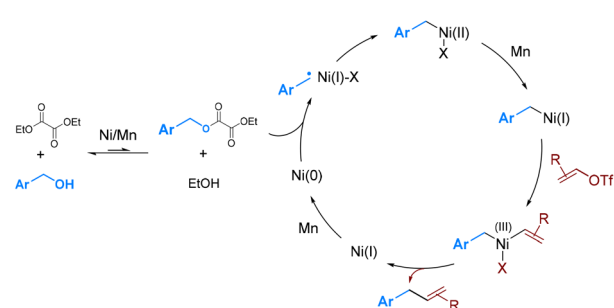
(c) Radical clock experiments



Scheme 4 Mechanistic studies. Standard conditions are as shown in Table 1, entry 1; see the ESI† for the reaction conditions; isolated yields are given for product **3c**; the yields were determined by NMR analysis using CH₂Br₂ as an internal standard for compounds **8**, **9**, and **11**.

formation of benzyl-H was significantly enhanced, whereas the homo-coupling of benzyl alcohol to dimer **9** was suppressed (Scheme 4b). (2) The reaction of **1c** with α -cyclopropylstyrene (**10**), a well-known radical clock substrate probe,¹¹ yielded a ring-opening and cyclization product **11** in 35% yield (Scheme 4c). These results suggest that the *in situ*-generated benzyl oxalates may be activated by nickel through a radical process.

Based on the above results, we proposed a catalytic cycle that is analogous to our previous proposal for the deoxy-arylation reaction (Scheme 5).^{6a} The transesterification between alcohol and diethyl oxalate produces a highly reactive oxalate. The reaction of benzyl oxalate with Ni(0), possibly *via* a radical process, generates benzyl-Ni(II)X.¹² Reduction of benzyl-Ni(II)X, followed by oxidative addition with alkenyl triflates, leads to



Scheme 5 Proposed mechanism.

the formation of benzyl-Ni(III)(Ar)X.¹³ Subsequent reductive elimination resulted in the formation of the coupling product.

Conclusions

In conclusion, we have developed a nickel-catalyzed dynamic kinetic cross-electrophile coupling reaction between benzyl alcohols and alkenyl triflates. This method enables the direct transformation of alcohols into structurally diverse benzyl-substituted cyclic alkenes. The reaction proceeds under mild conditions and exhibits good functionality tolerance with ester, phenol, indole, heterocycle, boronic ester *etc.* These findings expand the synthetic toolbox for deoxy-functionalization of alcohols. Further expansion of the scope of the dynamic kinetic cross-electrophile reaction is ongoing in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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